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PATENT SPECIFICATION

DRAWINGS ATTACHED



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COMPLETE SPECIFICATION

Coated Curved Glass Sheets

We, PITTSBURGH PLATE GLASS COMPANY, a corporation organised under the laws of the State of Pennsylvania, United States of America, of One Gateway Center, Pittsburgh 22, State of Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

The present invention relates broadly to filmed bent glass sheets and more particularly to an improved method of producing filmed bent glass sheets and various articles comprising such filmed bent glass sheets which are particularly suitable for window closures for vehicles, particularly automobiles.

It is known that metal oxide films may be deposited upon glass by applying a composition containing a metal salt such as stannic chloride to the surface of heated glass. Films of superior electrical conductivity may be produced by spraying plate, window or other glass while it is heated to a temperature above 400°F. but below the temperature at which the glass becomes molten, with tin tetrachloride or other tin salts in aqueous solution or in vapor state, in the presence of a reducing agent such as methanol, phenylhydrazine hydrochloride or other agents. The films thus obtained are of unknown composition, but appear to contain a preponderant amount, of the order of 97 to 99 per cent of a tin oxide and certain impurities which may include metallic tin, carbon, silicon, sodium and chlorine and other impurities, depending upon the composition of the applied tin-containing solution.

Articles having such films are useful in many fields. They have been found to be especially useful as viewing closures in automobiles, aircraft, trains and similar motive vehicles. In such use, bus bars are applied to the sheet filmed and the coating is placed

in series with a source of electrical potential through these bus bars. The coating is used as a heating element in order to heat the viewing closure and prevent the deposition of ice or fog thereupon.

Metal oxide films on glass panels are also suitable for reducing heat transmission by absorbing and reflecting a substantial portion of heat and other radiation incident on the panel. Various metal oxide films are capable of producing the desired results. By applying filming compositions having a metal salt or certain mixtures thereof capable of forming a metal oxide film according to the teachings of the prior art, films which moderate the radiant energy transmittance of viewing closures can be produced.

Typical metal oxide coatings having low heat transmissivity by virtue of high absorptivity and/or reflectivity are those containing tin oxide, indium oxide, cadmium oxide, or mixtures thereof, mixtures of tin oxide and antimony oxide with or without minor additions of the oxides of bismuth, iron, zinc, copper, vanadium, chromium, manganese, cobalt or mixtures thereof, iron oxide films with or without minor proportions of tin oxide, and titanium oxide films. Films containing cobalt oxide as a major ingredient with or without minor proportions of nickel oxide, mixtures of cobalt oxide with nickel and iron oxides, or mixtures of cobalt oxide with nickel and tin oxides, are particularly effective.

Such films having the property of screening heat rays are particularly useful when applied in the form of continuous bands extending across the upper portion of vehicle viewing closures, particularly windscreens, side-windows and rear windows of automobiles that have portions extending into the roof. With the use of increased areas of glass in automobiles, it has become necessary to insure that the viewing closures are

[Pn

capable of screening a relatively high proportion of the infrared radiation, especially in their upper portions, while improving the visibility in the portion of the vehicle where these additional areas of glass replace metal areas in modern automotive styles.

In accordance with the present invention there is provided a coated curved glass sheet particularly useful as a window closure having at least a portion thereof having a total energy transmissivity below 50 per cent. in which the reduced transmissivity is provided by a transparent non-iridescent metal oxide film having a thickness below 80 millimicrons on said portion of the sheet.

While the most common method of filming glass sheets with metal oxide films has been to heat the sheets and to spray filming compositions containing a salt of the metal to be oxidized upon contact with the heated glass surface, such films may also be formed by other methods, such as vaporizing a solution of a metal salt at reduced pressures or in vacuum and blowing the vapor on to the glass sheet; spraying a composition containing a salt of the desired metal or mixture of metal salts on to a cold glass sheet followed by heating the sheet to oxidize the metal salt to the oxide; applying a film forming metal salt in gaseous form by elevating its temperature to above its boiling point before its application; and sputtering or condensing a metal oxide on to a glass surface in a vacuum. Which method is employed in forming the metal oxide film is dependent upon the rate of production desired and the construction of equipment available.

According to a particular method for preparing the curved glass sheets of the present invention a glass sheet to be bent and coated is preferably first cut to the outline desired for the bent glass sheet. The film forming composition is then applied either to the entire sheet or to that portion only desired to be coated. The coated sheet is then mounted on a glass bending mold having an upper shaping surface conforming to the shape desired for the bent glass sheet, and subjected to glass-bending temperatures to cause the flat coated sheet to sag into conformity with the upper shaping surface of the bending mold.

If the sheet is to form a tempered window closure such as a rear window or side window of an automobile, it is subsequently tempered after the bending operation. If the sheet is to form part of a safety glass assembly such as a windscreen or side window, the coated sheet is mounted in alignment with another precut sheet that may either be coated or uncoated and both sheets are bent simultaneously with a suitable parting material interposed between the sheets to prevent their fusing together during the bending operation. After bending is com-

pleted, the matched glass sheets are laminated to opposite surfaces of a plastic interlayer.

According to the present invention, use has been made of metal oxide coatings which provide the necessary heat screening in thin layers while still maintaining sufficient transparency to light rays to be acceptable for a viewing closure. Such coatings are also free from haze and iridescence which are present in prior metal oxide films. The latter films have to be applied, to provide the necessary heat screening, in thicknesses approaching a quarter wave length of visible light, which results in iridescence. The thickness of such films also makes it very difficult for them to remain adherent to the glass sheet when the latter is bent, particularly on the concave surfaces. The properties of certain films in the various embodiments disclosed hereafter enable coated glass sheets to be bent to comparatively sharp curvatures without causing substantial deterioration of the films resulting from chipping or peeling from the glass surfaces during bending.

In the accompanying drawings forming part of the present disclosure.

Figure 1 is a plan view of a precut flat glass sheet of a typical rear window pattern (used in some United States 1957 automobiles) drawn to scale, showing the sheet coated with a continuous band of metal oxide film prior to bending;

Figures 2, 3 and 4 are cross sectional views along the line II—II of Figure 1, showing various embodiments of coated glass sheets prepared for bending, the thickness of the coating being exaggerated relative to the glass sheet;

Figures 5, 6 and 7 are cross sectional views of various embodiments of a typical windscreen provided with a band of metal oxide film in the upper portion thereof.

Figure 8 is a side elevation of one embodiment of apparatus for spraying vertically supported sheets.

Figure 9 is a sectional view taken along the lines IX—IX of Figure 8.

Figure 10 is a sectional view similar to Figure 9, showing how both surfaces of a glass sheet are sprayed simultaneously.

Figure 11 is a cross-sectional view of a horizontally disposed glass sheet bending mold shown passing a spraying gun according to still another embodiment of this invention.

Referring to Figure 1, a flat glass sheet is shown precut to the outline desired for the finally bent glass sheet and provided with a coating 12 of metal oxide. The coating may be in the form of a band as shown or may cover the entire surface of the glass sheet, according to the product to be fabricated. Figures 2 and 3 show the coatings applied to either the outer or inner surfaces, whereas Figure 4 shows a sheet coated on both surfaces.

TET 507.

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It is preferable to cut the sheets to the outline desired for the bent glass sheet before filming in order to be able to cut the maximum possible number of sheets from a large block of glass. If the blocks are cut to a rectangular shape before filming and then cut after the filming is completed, a lesser number of sheets are obtainable from a given area of glass, because a large amount of glass is wasted in cutting individual outlines from rectangular blocks. Since the upper portion of one precut outline nests somewhat into the bottom portion of its neighboring sheet, it is desirable to cut many sheets to outline from a larger block of glass.

Furthermore, since filming imposes a temper on the glass sheet when the glass is filmed by heating and spraying, if the glass is cut to the proper outline after filming by such a process (heating and spraying), the glass has to be cut while tempered. Tempered glass is difficult to cut. Hence, the entire operation is performed more efficiently by utilizing a single cutting operation to cut glass blocks into many flat sheets having the outline desired before filming.

The coating operation can be accomplished by causing relative movement between the glass and a spraying apparatus, and masking that portion of the glass sheet which is not desired to be coated if a continuous band is to be applied. Alternatively, the entire glass sheet may be coated and then portions removed from the areas desired to remain uncoated. The former method is preferred where only a band of film is desired.

When it is desired to have a horizontal line of demarcation between the coated and uncoated portions of the glass in a vehicle viewing closure, the mask employed between the source of the filming composition and the glass sheet to be coated is curved to compensate for the curvature and tilting imparted to the coated glass sheet when the latter is bent and installed in a frame.

The mask may be either applied to the portions of the sheet to be kept free from coating or may be fixed to the spraying apparatus. The latter alternative may require that the spray apparatus be translated or reciprocated in a direction transverse to the longitudinal dimension of the sheets to be coated if the sheets are moved continuously past the spraying apparatus. The spray apparatus may be fixed in position and the sheets moved in steps, with the spraying accomplished only when sheets are positioned properly. The number of spray guns needed depends on the area to be coated.

While single sheets of glass have been provided with films in the form of bands extending completely across the upper portion of the viewing closure as mounted in the frame to provide selective screening of the heat rays while still permitting light

transmittance, other uses for similar structures have been suggested. For example, when a band covering a portion of the surface or when a continuous film covering an entire surface of a bent glass sheet is both electroconductive and transparent, the article is suitable for use as a radio antenna as well as a window closure for the vehicle.

In automobile windscreens and certain other vehicle closures wherein curved glass sheets are laminated to opposite surfaces of a plastic interlayer, the provision of a coating of metal oxide on at least one of the surfaces of one of the curved glass sheets in the form of a band extending across the upper portion of the viewing closure panel provides a means for shielding the interior of the vehicle from heat rays while permitting light rays to be transmitted. An example of such a structure is shown in Figure 5 wherein a curved glass sheet 10 provided with a coating 12 is laminated on one side of a plastic interlayer 14 and another curved sheet of glass 16 is laminated to the opposite surface of the plastic interlayer. The laminated assembly comprises an upper portion 18 and a bottom portion 20. The upper portion 18 forms the part of the viewing closure that includes a horizontal area extending into the roof and the upper portion of the vertically oblique area of a viewing closure such as a windscreen. Note that the coating is limited to the upper portion 18 and does not extend into the uncoated bottom portion 20 of the windscreen, which is located at the driver's eye level. In Figure 6, the band of metal oxide coating is located on the outer surface of the outer sheet of the laminate. The laminate of Figure 7 shows both inner and outer surfaces of the outer sheet coated.

In coating glass sheets preparatory to bending the coated sheets, various metal oxide films have been found to be quite suitable. However, certain films containing cobalt oxide as a major ingredient, namely, containing from about 50 per cent by weight of cobalt oxide up to in excess of 99 per cent by weight, have been found to be superior for heat shielding properties. These cobalt oxide films have been found to have their permanence improved by incorporation therein of some nickel oxide as disclosed in United States Patent No. 2,688,565. Other additives found suitable to add to cobalt oxide films that either contain the nickel oxide or are free from nickel oxide include iron oxide and tin oxide in minor proportions, not exceeding 5 per cent by weight of the metal oxide coating. The cobalt oxide constituent of these films may be either CoO , Co_2O_3 or a mixture of both oxides.

The estimated thickness of such coatings required to reduce by 25 per cent the transmission of the incident infrared rays is of about 50 millimicrons and less, considerably

below the thickness required for the same reduction in transmission by other films as estimated from their interference colors. These coatings are especially desired by automobile manufacturers because of their neutral shade and their freedom from iridescence by virtue of their thinness.

FILMING APPARATUS

Referring to Figures 8 and 9, a typical spray apparatus will be described. The apparatus includes a pair of spray guns 30, each secured to a bracket housing 31 carried by a vertical post 32. The posts 32 are adjusted vertically within sleeve supports 33. An expansion spring 34 is wound about each post 32 to extend between a bracket housing 31 and a sleeve 33. Bracket housings 31 are pivotally adjustable about posts 32, their orientation being fixed by set screws 35. Flanges 36 at the bottom of posts 32 and flanges 37 at the top of sleeves 33 cooperate to provide stops limiting upward movement of the spray gun support posts.

The spray guns are provided with baffle plates 38 secured to the supporting structure of the gun by means of a baffle support structure 39. The purpose of baffles 38 is to delineate one boundary of the spray.

The spraying apparatus includes a carriage 40 for conveying the glass sheets through a heating Lehr and a spraying station. The carriage is supported by an overhead monorail 42 and includes tongs 44 which grip the upper edge of glass sheets 10 to carry the latter through the glass treating apparatus.

The carriages also include a cam rail 46 curved longitudinally of the monorail. Depending supports 48 secured at their upper ends to the overhead portion of the carriage support the cam rail in its desired position in alignment with the top of the pivoted spray guns. The bracket housings 31, the posts 32 and the spray guns 30 are urged upwardly against the cam rail 46 by springs 34.

The purpose of the curved cam rail 46 and its supporting structure 48 is to control the vertical position of the spray relative to the passing sheet so that the cut-off line between the coated and uncoated areas is curved in such a manner that when the sheet is subsequently bent and installed in an automobile frame, it has a substantially horizontal cut-off line between the coated and uncoated regions. A different shaped cam is required for each separate pattern to produce a cut-off line that is exactly horizontal in the installed sheet. Therefore, the cam and its supports are so constructed that they are easily detachable from the overhead carriage.

It has been found that the cut-off line of moderately bent sheets does not depart too greatly from a straight horizontal cut-off line when the sheets are translated past a fixed spray gun. In such cases, the cam rail 46 and its support 48 are omitted and the

vertical support posts 32 fixed to sleeves 33.

In spraying vertically supported sheets, it has been found desirable to orient one of the spray guns at an upward angle of about 30 degrees with the plane of the glass sheet and the other spray gun at an angle less than 30 degrees. Figure 10 shows how the vertical support apparatus can be used to coat bands of film on the upper edges of opposite surfaces of a glass sheet. The spray guns are angled upwardly as in the previous embodiments to avoid the possibility that drippings will contact the sheets.

In the embodiments of Figures 8, 9 and 10, the sheet is conveyed on a monorail 42 through a heating zone where the glass temperature is raised to at least 400°F. and below the temperature at which the glass becomes molten. The heated sheet is then conveyed past the spraying guns at a speed sufficient to form a band of film having a thickness below 80 millimicrons, preferably from about 40 to 50 millimicrons in order to avoid iridescence, and to minimize film crazing when the filmed sheet is subsequently bent to sharp curvatures, i.e. about 9 inch radius of curvature or less.

Another spraying method found to be quite suitable for large scale production comprises mounting the flat glass sheet 10 on a support mold 60 (Fig. 11) having a continuous rail 62 braced by reinforcing rods 64. In such apparatus, the glass sheet 10 is conveyed horizontally through a heating Lehr where the sheet is heated to the proper temperature and then moved past one or more spray guns 30. The spray guns 30 are oriented to direct the spray along a central axis disposed at an acute angle to the sheets transversely of their longitudinal dimension. A baffle sheet 66 has been found necessary to prevent drippings from the spray guns from falling on the uncoated portion of the glass sheet. The baffle sheet is interposed between the spray gun and the path of movement of the uncoated portion of the glass sheet.

In Fig. 1 it is shown that the film produced varies in thickness from a minimum along a line intersected by an edge of said spray traversing the shortest possible straight line distance from the point of origin of the spray to the coated portion and increasing transversely of the longitudinal axis of the sheet to a maximum along an edge of the sheet included in the portion directly exposed to the spray. This method of spraying the glass sheet is claimed in our Divisional Application No. 26928/59 (Serial No. 866,333) as a method of providing a glass sheet with a non-uniform metal oxide film by spraying on to the sheet heated to a temperature above 400°F. and below the softening temperature of the sheet a film forming composition capable of producing a metal

oxide film thereon which comprises orienting said sheet in a fixed plane, applying said spray from a point of origin spaced from the plane of said sheet to a portion of said sheet, maintaining said spray about a central axis having a fixed oblique angular relationship to the plane of said sheet, and providing relative motion between the heated oriented sheet and the spray transverse to a line which is the projection of the central axis of the spray on the sheet so that a film of non-uniform thickness is formed on the sheet, said thickness varying from a minimum along said line of intersection from an edge of said spray traversing the shortest possible straight line distance from the origin of said spray to the coated portion and increasing to a maximum along an edge of the sheet included in the portion directly exposed to said spray. After the sheets are coated by spraying whether by the vertical or horizontal techniques described above, they are allowed to cool sufficiently to be handled and then are mounted on conventional sectionalized bending molds and subjected to a bending operation.

EXAMPLE I.

Glass sheets having a nominal thickness of $\frac{1}{8}$ inch and a composition consisting essentially of the following parts by weight:

SiO—71.47%
 Na₂O—13.11% (including about 0.5% K₂O impurities).
 CaO—11.67%
 MgO—2.40%
 Na₂SO₄—0.48%
 NaCl—0.12%
 Al₂O₃—0.19% (including about 0.02 to 0.03 TiO₂ and about 0.01% Zr₂O₃ impurities).
 Fe₂O₃—0.56%

were coated with various heat absorbing metal oxide film forming compositions. The glass sheets were heated for about five minutes in a tunnel-like furnace held at a controlled temperature of 1180°F. The sheets were supported at their upper ends by means of tongs suspended from monorails. For flat glass sheets approximately 32 inches wide and 71 inches long cut to the pattern desired for an automobile rear window, about 50 grams of composition were sprayed on each plate coated. The suspended glass sheets were moved out of the heating furnace and moved past fixed spraying guns at a speed of about 12 inches per second.

The guns were directed on a section about 9 inches wide along the top edge of the plate. These guns were angled upwardly and the sprays therefrom contacted the plate at about a 30 degree angle with the glass surface.

Two guns were used. In some instances one of the two guns was directed at a smaller angle than 30 degrees with the glass surface. A shield was used to baffle the lower portion of the glass from the spray. Shielded spray guns so disposed produced bands in the upper portion of the coated glass sheets having slightly graduated thicknesses and a moderately sharp cut-off. After the spraying operation was completed, the glass sheets were mounted on bending molds and conveyed transversely through a bending lehr in the manner presently accomplished in the glass bending art.

EXAMPLE II

The glass sheets have also been sprayed after mounting on a horizontal edge support structure. The plate, after travelling through a lehr-type furnace, was moved past a spray gun set-up where the spray was applied at an acute grazing angle relative to the horizontally disposed glass sheet. After the band of coating was applied, the sheets were removed from the support and placed upon conventional bending molds and conveyed through a horizontally disposed bending lehr.

EXAMPLE III

Glass sheets have also been coated by heating the sheet and then spraying the heated sheet with a filming composition sprayed from a moving gun directed at a low grazing angle toward the zone where coating was desired. The filmed sheets were then mounted on sectionalized bending molds and bent according to current practices involving conveying the glass laden mold through a lehr, gradually heating the sheet to glass softening temperature and causing the sheet to conform to an upper mold shaping surface by a combination of heat sagging and mechanical force.

After the sheets were coated and bent, the thickness of the films formed was estimated by referring to the experience gained from experiments listed below, the color of the film noted, its visible-light transmittance determined by photo metric reading and total energy transmittance estimated by use of a projector lamp disposed on one side of the coated sheet and a thermopile located at the other side. The following Table I shows various filming compositions and the absorption characteristics of the films formed from such compositions. The nature of the filming composition, particularly the cation of the metal salt, determined the thickness needed to produce a film having the desired reduced transmission coefficient. Varying the filming technique between that of Examples I, II and III did not affect the film characteristics appreciably.

TABLE I
FILMING COMPOSITIONS

	Thick- ness Milli- microns	Color	Visible Trans- mittance	Total Energy Trans- mittance
5				
1. 600 grams ethyl alcohol—(C_2H_5OH) 200 grams cobalt acetate—(CH_3COO) ₂ Co 60 grams acetic acid—(CH_3COOH)	40—50	Silvery to Colorless	26%	24%
10 2. Composition 1 plus 20 grams nickel acetate—(CH_3COO) ₂ Ni	40—50	Silvery to Colorless	27%	22%
3. Composition 2 plus 4 grams ferric acetate—(CH_3COO) ₃ Fe	40—50	Silvery to Colorless	26%	19.5%
15 4. 75 grams methyl alcohol—(CH_3OH) 7.5 grams acetic acid—(CH_3COOH) 25 grams cobalt acetate—(CH_3COO) ₂ Co	40—50	Silvery to Colorless	26%	22%
5. Composition 4 plus 2.5 grams nickel acetate—(CH_3COO) ₂ Ni	40—50	Silvery to Colorless	26%	19%
20 6. Composition 5 plus 0.5 gram ferric acetate—(CH_3COO) ₃ Fe	40—50	Silvery to Colorless	25%	19%
7. 73 grams stannic chloride 20 grams antimony trichloride 15 grams hydrochloric acid (37%) 70 grams water	240	Red	26%	20%
25 8. 73 grams stannic chloride 12 grams antimony trichloride 15 grams bismuth chloride 15 grams hydrochloric acid 70 grams water	400	Red	27%	17%
30 9. 2250 cubic centimeters stannic chloride 1765 cubic centimeters water 565 cubic centimeters methyl alcohol 160 grams phenyl hydrazine hydrochloride 230 cubic centimeters aqueous solution containing 10% by weight of dioctyl sodium sulfo succinate	900—1000		52%	30%

The following experiments were performed to establish the thickness of silvery, non-iridescent films formed by applying compositions 1 to 6 above. It has already been established that the interference colors present in thin films are indicative of the film thickness. The thickness of iridised films may be gauged by the apparent color of the film caused by interference of light reflected therefrom. As the thickness of the film increases, its apparent color changes and the order or succession of the colors with increasing thickness is analogous to that of the well known Newton rings described in "A Treatise on Light", R. A. Houston, Longmans, Green & Company, Ltd., (1938), page 147.

Thicker films have less transmission than thinner films. Simple calculation shows that the first order red corresponds to a thickness of approximately 80 millimicrons. By comparing the color of iridescent and non-iridescent films of different thicknesses with the percentage transmission of visible light through the filmed glass samples, it was concluded that the silvery, non-iridescent films must have a thickness below 50 millimicrons.

TABLE II

Color	Visible Trans- missivity	Thickness	
Silvery	24%	40-50 millimicrons	65
Non-iridescent		(estimated)	
Amber	19-20%	60 millimicrons	70
Non-iridescent		(estimated)	
Red (1st order)	16-17%	80 millimicrons	
		(calculated)	
Green	10-11%	200 millimicrons	75
(2nd order)			
Iridescent			
Red (2nd order)	6-7%	230 millimicrons	
Iridescent			
Green	4-5%	330 millimicrons	80
(3rd order)			
Iridescent			

The glass composition used for the coated articles has some effect on the relative transmission. The following Table III discloses the relative efficiency of clear plate glass coated with a coating of the type formed by spraying a composition containing cobalt acetate with similar compositions sprayed on tinted glass. Tinted glass compositions differ from the clear glass principally by the

amount of iron oxide contained in the glass composition as shown in Table IV.

TABLE III

Film	Glass	Transmittance		
		Visible-light	Total Solar Ultra-violet	Total Solar Infrared
10	3 Tinted	24.2%	8.2%	12.5%
	5 Tinted	22.1%	7.2%	11.0%
	4 Clear	26.9%	14.5%	40.3%

TABLE IV

TYPICAL CLEAR AND TINTED GLASS COMPOSITIONS

Ingredient	Clear		Tinted	
	(weight)		(weight)	
SiO ₂	70-75%		70-75%	
Na ₂ O	10-15%		10-15%	
CaO	5-15%		5-15%	
20 MgO	2-10%		2-10%	
Fe ₂ O ₃	0 to 0.2%		0.25-1%	

From the above experiments it is obvious that the harmful ultraviolet and infrared radiations may be screened out more effectively when tinted glass is coated with the coating utilized than when clear glass is coated with the same coating. Furthermore, such beneficial screening is accomplished with only a slight effect on the transmission of visible light through the coated glass assembly.

Films having the superior heat screening properties have been formed by spraying compositions that include an organic cobalt salt as a major ingredient. These films have been studied by X-ray diffraction and electron microscope techniques and appear to be composed of sub-microscopic amorphous particles. While their chemical composition is unknown, it is believed that cobalt oxide forms a major ingredient of the film composition.

The present invention has provided a novel method of producing articles comprising curved coated glass sheets involving first coating at least an area of the sheet and then bending the coated sheet. A particularly outstanding utility is obtained from this inventive concept when low heat transmission films having visual transparency are formed in thicknesses less than 80 millimicrons by spraying film forming compositions containing organic cobalt salts on to heated glass sheets before bending the latter. Such bent coated sheets are especially suitable for use as vehicle window closures, especially when the coating is in the form of a band extending across the upper portion of the bent sheet.

The superior coatings formed by spraying compositions 1 to 6 have been tested in an accelerated test machine where the coatings have been subjected to thousands of hours of accelerated testing involving alternate ultraviolet irradiation and water spraying,

estimated to be equivalent to 10 years normal exposure without appreciable deterioration of the film.

Having regard to the provisions of Section 9 of the Act, attention is drawn to the claims of Patent No. 822,295.

WHAT WE CLAIM IS:

1. A coated curved glass sheet particularly useful as a window closure having at least a portion thereof having a total energy transmissivity below 50 per cent, in which the reduced transmissivity is provided by a transparent non-iridescent metal oxide film having a thickness below 80 millimicrons on said portion of the sheet.
2. A glass sheet according to claim 1, in which the film provides a continuous band on the surface of said sheet.
3. A glass sheet according to claim 1 or 2, which is composed of a soda-lime-silica glass containing between 0.25 per cent and 1 per cent by weight of iron oxides.
4. A glass sheet according to any one of the preceding claims, in which the film contains cobalt oxide as a major ingredient.
5. A method of making a curved glass sheet having a portion coated with a metal oxide film, which comprises first applying a metal oxide film forming composition to a surface of a flat glass sheet and then heating the flat glass sheet to glass softening temperatures, thereby causing the sheet to sag to a predetermined curvature and the formation of a metal oxide film bonded to the glass surface, the amount of composition applied being sufficiently small to produce a metal oxide film having a thickness below 80 millimicrons but sufficiently great to reduce the transmissivity of the coated portion to no more than 50 per cent.
6. A method according to claim 5, in which the coated bent sheet is tempered after it is coated and bent.
7. A method according to claim 5 or 6, in which the glass sheet is cut into its ultimate outline before the film forming composition is applied.
8. A method according to any one of claims 5 to 7, in which the film forming composition contains a cobalt salt capable of forming a heat absorbing film containing cobalt oxide as a major ingredient.
9. A method according to any one of claims 5-8, in which the film forming composition is applied by spraying and which comprises orienting the glass sheet in a fixed plane, applying the spray from a point of origin spaced from the plane of said sheet to a portion of said sheet, maintaining said spray about a central axis having a fixed oblique angular relationship to the plane of said sheet, and providing relative motion between the oriented sheet and the spray transverse to a line which is the projection of the central axis of the spray on the sheet

- so that the metal oxide film formed thereon is of non-uniform thickness, said thickness varying from a minimum along said line of intersection from an edge of said spray
- 5 traversing the shortest possible straight line distance from the origin of said spray to the coated portion and increasing to a maximum along an edge of the sheet included in the portion directly exposed to said spray.
- 10 10. A method according to claim 9, wherein the sheet is moved in a horizontal path through the spray at a constant linear velocity.
- 15 11. A method of making a coated curved glass sheet according to claim 1 substantially as herein described.
12. A coated curved glass sheet produced according to any one of claims 5 to 11.
13. A coated curved glass sheet substantially as herein described with reference 20 to the Examples.
14. A window closure, such as an automobile rear window, comprising the glass sheet according to any one of claims 1 to 4, 12 or 13. 25
15. An automobile windscreen comprising a pair of curved glass sheets, and a clear, transparent, plastic interlayer disposed between said curved sheets, in which at least one of the sheets is the sheet according to any one of claims 1 to 4, 12, or 13 with the film bonded to and extending across said sheet in intimate contact with the surface thereof. 30

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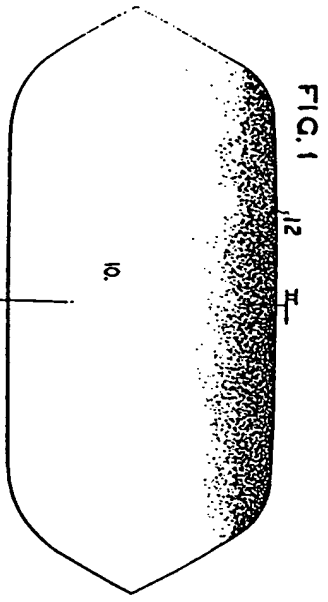


FIG. 1

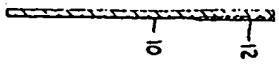


FIG. 2



FIG. 3

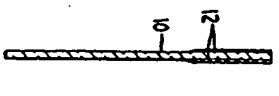


FIG. 4

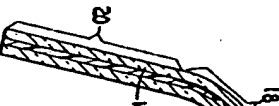


FIG. 5

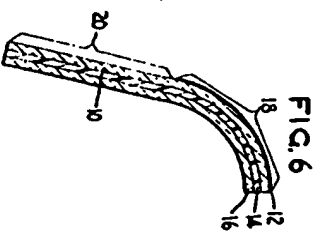


FIG. 6

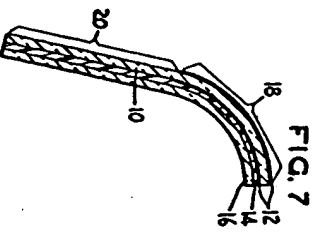


FIG. 7

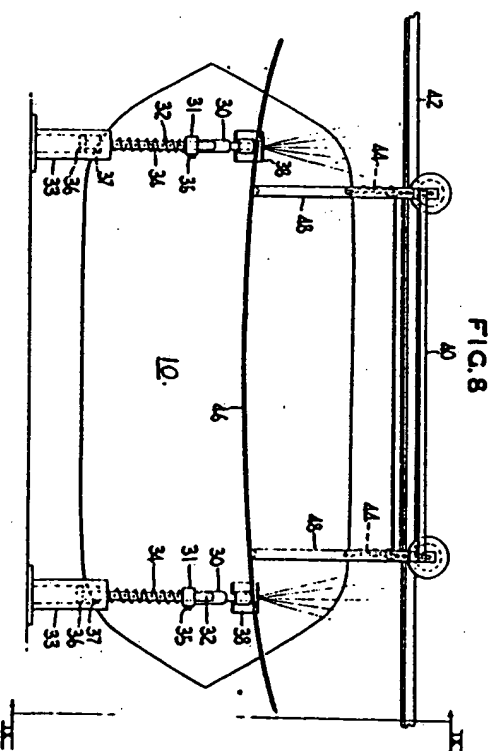


FIG. 8

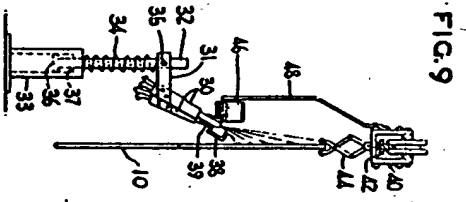


FIG. 9

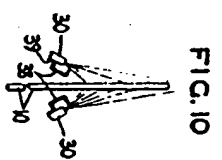


FIG. 10

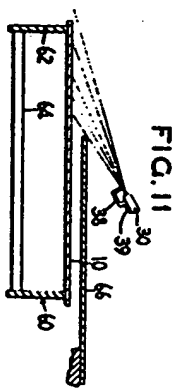


FIG. 11